

SHORT
COMMUNICATIONS

Uncommon C¹–C² rupture in Methyl-4-C-allyl-2,4-dideoxy-3-O-mesyl- α -D-arabino-hexopyranoside

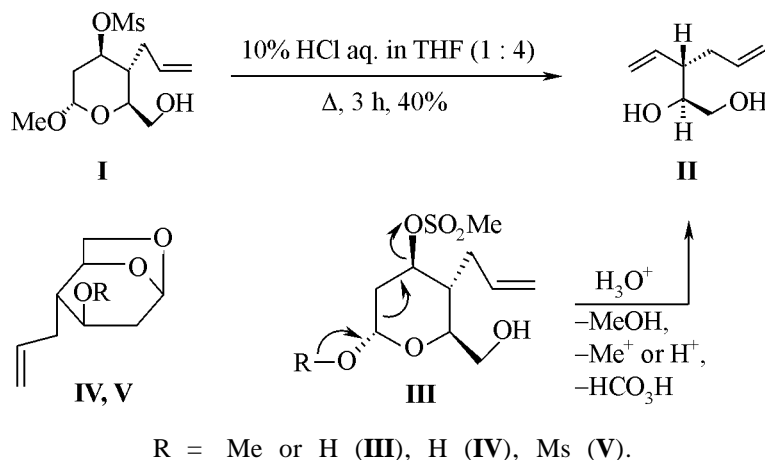
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In the course of a “rigorous” water-acidic deprotection of methoxyacetal function in a 2-deoxy-3-O-mesyl derivative of D-glucose (**I**) we observed a slow process providing in a moderate yield a new fragmentation product, diol **II**. According to TLC data in the reaction mixture appeared also an intermediate compound more polar than diol **II**, presumably the expected lactol **III**. However a considerable

tarring did not allow an unambiguous conclusion that diol **II** formed via lactol **III** corresponding to acetal **I**. Apparently this process occurs by a concerted mechanism formally similar to Grob fragmentation [1, 2] as shown on the hypothetical scheme. Note that the methylglucoside (**I**) used in this study (α : β , 9:1) was prepared from the known alcohol **IV** [3] by standard procedures of mesylation and methanolysis.



(2S,3S)-(-)-3-Vinylhex-5-ene-1,2-diol (II). A solution of 0.1 g (0.70 mmol) of mesylate **I** in a mixture of 10% aqueous HCl and THF (1:4) was boiled for 2 h. To the reaction mixture a saturated water solution of NaHCO₃ was added to pH 7, and the reaction product was extracted into dichloromethane (3 × 5 ml). The combined organic extracts were dried with MgSO₄, evaporated, and the residue was subjected to column chromatography on SiO₂ (eluent ethyl acetate–hexane, 2:1). We isolated 0.02 g (~40%) of oily compound **II**. $[\alpha]_D^{20}$ -1.5° (c 0.5, CHCl₃). IR spectrum, cm⁻¹: 3400, 3050, 1640, 1080,

920. ¹H NMR spectrum, δ , ppm: 2.10–2.40 m (5H, CH₂, CH, 2OH), 3.50–3.80 m (3H, CH₂O, CHO), 5.00–5.20 m (4H) and 5.65–5.83 m (2H) (2CH=CH₂). ¹³C NMR spectrum, δ , ppm: 35.56 (C⁴), 46.82 (C³), 64.93 (C¹), 73.20 (C²), 116.11, 116.58 (C⁶, CH₂=), 136.19, 137.93 (C⁵, CH=).

Methyl-4-C-allyl-2,4-dideoxy-3-O-mesyl- α -D-arabino-hexopyranoside (I). A solution of 0.6 g (2.42 mmol) of mesylate **V** in 5 ml of a 10% solution of gaseous HCl in MeOH was stirred for 3 h, neutralized with NaHCO₃, and evaporated. By

column chromatography on SiO₂ (eluent ethyl acetate-hexane, 1:1) 0.48 g (80%) of oily compound **I** was isolated containing 5–10% of the respective β-anomer. $[\alpha]_D^{20} +22^\circ$ (*c* 1.0, CHCl₃). IR spectrum, cm⁻¹: 3500, 3030, 1650, 1360, 1180, 920, 780. ¹H NMR spectrum, δ, ppm: 1.90 m (2H, H², H⁴), 2.20–2.40 m (4H, CH₂, H², OH), 2.99 s (3H, SO₂CH₃), 3.28 s (3H, OCH₃), 3.60–3.80 m (3H, H⁵, 2H⁶), 4.80 t (1H, H¹), 4.95 m (1H, H³), 5.05–5.20 m (2H) and 5.80 m (1H) (CH=CH₂). ¹³C NMR spectrum, δ, ppm: 30.54 (CH₂), 37.07 (C²), 38.67 (SO₂CH₃), 40.60 (C⁴), 54.55 (OCH₃), 62.36 (C⁶), 70.87 (C⁵), 97.96 (C¹), 117.87 (CH₂=), 133.58 (CH=).

4-C-Allyl-1,6-anhydro-2,4-dideoxy-3-O-mesyl-β-D-arabino-hexopyranose (V). To a solution of 0.5 g (2.94 mmol) of alcohol **IV** in a mixture of 3 ml of CH₂Cl₂ and 0.6 ml of triethylamine was added dropwise a solution of 0.26 ml of mesyl chloride in 1 ml of CH₂Cl₂. On completion of the reaction (TLC monitoring) 5 ml of saturated NaCl solution was added to the reaction mixture, and the product was extracted into CH₂Cl₂ (3 × 15 ml). The combined

organic extracts were dried with MgSO₄, evaporated, and the residue was subjected to column chromatography on SiO₂ (eluent ethyl acetate-hexane, 1:2). We obtained 0.68 g (94%) of mesylate **V**. $[\alpha]_D^{20} -57^\circ$ (*c* 1.0, CHCl₃). IR spectrum, cm⁻¹: 3020, 1640, 1350, 920. ¹H NMR spectrum, δ, ppm: 2.00–2.10 m (3H, 2H², H⁴), 2.20–2.50 m (2H, CH₂), 3.02 s (3H, SO₂CH₃), 3.80 d.d (1H, H^{6-exo}, *J* 5.3, 7.0 Hz), 4.22 d (1H, H^{6-endo}, *J* 7.0 Hz), 4.40 d (1H, H⁵, *J* 5.3 Hz), 4.72 m (1H, H³), 5.10–5.20 m (2H, CH₂=), 5.52 s (1H, H¹), 5.75–5.90 m (1H, CH=). ¹³C NMR spectrum, δ, ppm: 33.82 (CH₂), 34.89 (C²), 38.82 (SO₂CH₃), 43.03 (C⁴), 67.47 (C⁶), 73.79 (C⁵), 76.48 (C³), 99.30 (C¹), 118.16 (CH₂=), 134.80 (CH=).

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